



Fabrication and Characterization of Blue Organic Light-emitting Diodes

**by Merric Srour, Richard Fu, Steven Blomquist, Jianmin Shi,
Eric Forsythe, and David Morton**

ARL-TR-5773

September 2011

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory

Adelphi, MD 20783-1197

ARL-TR-5773**September 2011**

Fabrication and Characterization of Blue Organic Light-emitting Diodes

**Merric Srour, Richard Fu, Steven Blomquist, Jianmin Shi,
Eric Forsythe, and David Morton
Sensors and Electron Devices Directorate, ARL**

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY) September 2011		2. REPORT TYPE Final		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Fabrication and Characterization of Blue Organic Light-emitting Diodes				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Merric Srour, Richard Fu, Steven Blomquist, Jianmin Shi, Eric Forsythe, and David Morton				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-SEE-E 2800 Powder Mill Road Adelphi MD 20783-1197				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-5773	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>Organic light-emitting diode (OLED) technology has demonstrated high efficiency and brightness, leading to a strong commercial interest. One remaining problem with the OLED technology is the efficiency and color saturation for blue light emitters. A series of experiments were developed to test the brightness and light disposition of organic films. The different combinations of N,N'-Bis- (1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), 1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI), and doping cesium carbonate (Cs₂CO₃) were investigated to determine which recipe results in brighter luminance and greater longevity.</p>					
15. SUBJECT TERMS Organic Light-Emitting Diodes (OLED), organic film					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 22	19a. NAME OF RESPONSIBLE PERSON Richard Fu
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (301) 394-1473

Contents

List of Figures	iv
List of Tables	iv
1. Introduction	1
2. Approach	1
2.1 Process of Purifying Organic Chemicals.....	1
2.2 OLED Substrate Preparation	2
2.3 Device Structure	5
2.4 OLED Fabrication	6
2.5 OLED Characterization	7
3. Results and Discussion	11
4. Conclusions	13
5. References	14
List of Symbols, Abbreviations, and Acronyms	15
Distribution List	16

List of Figures

Figure 1. Equipment was used for purifying organic chemicals.	1
Figure 2. Ultrasonic equipment.....	3
Figure 3. Diagram of DI H ₂ O and IPA fill lines.	4
Figure 4. O ₂ plasma equipment used to clean the ITO patterned glass substrates.....	5
Figure 5. OLED device structure.	5
Figure 6. Equipment used to make OLED.....	7
Figure 7. Equipment used to test and measure OLED (<i>I</i>).	8
Figure 8. Example picture of LabView (<i>I</i>).	9
Figure 9. Front side of a blue OLED being tested.	10
Figure 10. Back side of a OLED being tested (the black cap is placed there to keep any moisture from affecting the OLED).....	10
Figure 11. I-B graph.....	12
Figure 12. Emission spectra of the blue OLED.	12
Figure 13. I-V curve.....	13

List of Tables

Table 1. TPBI purification temperature and time schedule.	2
Table 2. Organic material thickness.....	6
Table 3. Results of blue OLED measurement (all the numbers were taken from 20 mA/cm ²)....	11

1. Introduction

In 1987, an American chemist Van Slyke and an American physical chemist Ching Tang reported for the first time on an organic electroluminescent device obtained by using a multilayer structure with an organic film as an emitter (1, 2). Organic light-emitting diodes (OLEDs), unlike regular light-emitting diodes (LEDs), have several advantages: lightweight, wide view angle, high luminance, large emitting surface, full color, and low power consumption.

OLEDs are the future for most electric devices with a display. This new technology is currently being researched by many companies including LG, Samsung, and Sony. It is also being researched by the military to help and protect the lives of Soldiers.

The Flexible Display Team at the U.S. Army Research Laboratory (ARL) is working closely with many other laboratories and companies to research and fabricate flexible displays. The team at ARL is researching OLEDs for military applications. This report goes through the steps for fabricating and characterizing OLEDs, starting with purifying the organic chemicals to fabricating the OLED to characterizing an OLED's properties.

2. Approach

2.1 Process of Purifying Organic Chemicals

Before organic chemicals are used to make an OLED device by thermal evaporator, those chemicals have to be purified. Figure 1 shows the equipment used during the purification process.

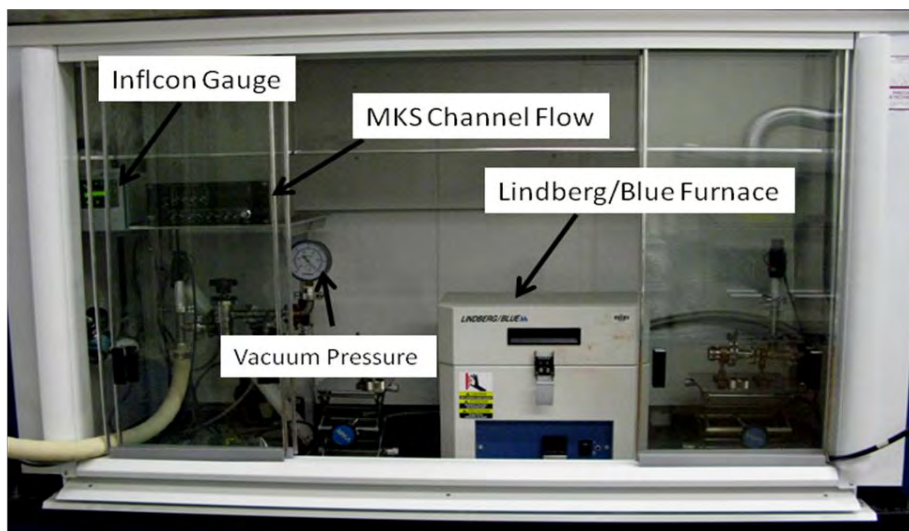


Figure 1. Equipment was used for purifying organic chemicals.

The following steps outline the purification process:

1. Load the non-pure materials into the glass boat.
2. Put the glass boat into the glass tube.
3. Stuff one end with the “fiberglass and micron” seal.
4. Put the glass tube into the Lindberg/Blue furnace (make sure the boat is laying on the piece of thermocouple in the middle, which measures the temperature).
5. Adjust the “stands” until both sides of the glass tube are lying loosely on the side of the furnace, then hold the tube (so the boat does not turn and flip over) and screw tightly.
6. Slowly open the gate valve, watch the pressure gauge rise from 0 to 30, and then turn the knob two more turns to make sure that the gate valve is fully open.
7. Turn the MKS power, channel 1, and flow 1 on.
8. Watch the Inficon gauge until it’s steady, then turn MKS channel one, N2 flow on and off three times to stabilize the pressure.
9. Turn the heater to 200 °C for 30 min and following schedule in table 1 for 1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBI) purification .
10. The pressure gauge gas flow should be as follows:
 - Ch 1 – 1.5×10^{-1}
 - Ch 2 – 1.0×10^0

Table 1. TPBI purification temperature and time schedule.

Temperature (°C)	Time
1. 200	30 min
2. 250	30 min
3. 300	30 min
4. 350	Until fully crystallized

2.2 OLED Substrate Preparation

After acquiring all the right organic chemicals, one loads them into the machine so that they can be inserted on the indium titanium oxide (ITO) glass substrate.

This section explains the cleaning process for the 2-in ITO glass substrates. Each piece of glass must be pre-cleaned in a multi-step rigorous cleaning process. The ITO patterned glass was purchased from Polytronics Inc.

The process for cleaning the ITO patterned glass is as follows:

1. Prepare six cleaning beakers with deionized water (DI H₂O) and soap (use 400-ml beakers for 2.5 substrates and 250-ml beakers for 2.0 substrates).
2. Mark each glass substrate on the back with the run number and trial number. To remove photoresist do the following:
 - a. Use two separate beakers (not the cleaning beakers), one with DI H₂O and isopropyl alcohol (IPA) and another with acetone.
 - b. Put one substrate in the acetone beaker in the ultrasonic system (figure 2).

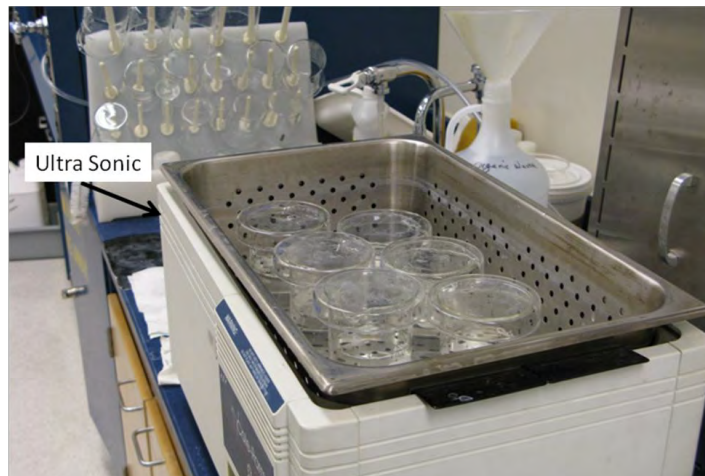


Figure 2. Ultrasonic equipment.

- c. Using a rolled-up soft cloth, rub the device area to remove the photoresist (while sonicating).
 - d. Put the substrate into the DI H₂O plus IPA—do not let the glass substrate dry when transferring it from the acetone to the DI H₂O and IPA.
 - e. Put the substrate into DI H₂O plus soap and sonicate for 5 min.
 - f. Repeat steps b through e with the same solution, doing all six substrates
3. Remove the substrates from cleaning beakers, one at a time, and scrub the substrates on both sides twice with a tooth brush dipped in soap and water.
4. Put the substrates back into the beakers and return the beakers to the ultrasonic bath. Sonicate for 5 min.
5. Repeat steps 3 and 4 for all the substrates.
6. Starting with the first substrate that was scrubbed, remove the beaker from the bath and run DI H₂O through the beaker three times.

7. Fill the beaker with DI H₂O above the device area (up to the red line in figure 3).
8. Fill to the top of the substrate with IPA (up to the green line in figure 3).
9. Repeat steps 7 thru 8 for all substrates and sonicate for around 5 min.
10. Dump the DI H₂O and IPA.
11. Quickly refill the beaker with proportions of DI H₂O and IPA as described in figure 3.

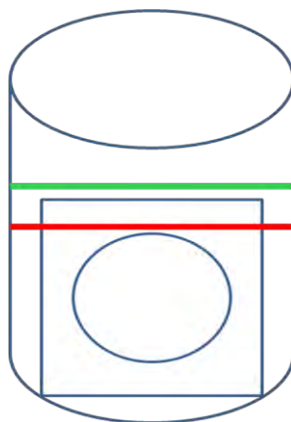


Figure 3. Diagram of DI H₂O and IPA fill lines.

12. Sonicate the substrates again for 5 min.
13. Remove the substrates one at a time, take them to the hood, blow dry, and place them in a clean substrate holder.
14. The following is the process to perform the O₂ plasma treatment (figure 4):
 - a. Turn on the pump and the main power switch. Make sure the CFx gas valve is off and that the oxygen valve is open (counterclockwise) all the way.
 - b. Load the substrates into chamber, ITO-side up. Some overlapping is OK near the substrate edges. Close and latch the door.
 - c. Hold the preset button and adjust the control knob for 100 W of power. Set the timer to read C 600 S.
 - d. Flip up the standby switch. This will pump down the chamber. As the pressure drops, the needle will slow down below 8×10^{-2} Torr (this takes approximately 1 min).
 - e. At this point, press the start button and flip down the standby switch. The oxygen will flow and the pressure should stabilize around 700 mTorr. In around 30 s, the plasma will commence.

- f. Check and adjust the power. Flip the forward/ reverse switch to check the reverse power. Adjust the matching network if not zero
- g. At the end of the run, the barrel will come to an atmospheric level and the tool will start to beep. Open the door to stop the beeping and retrieve the substrates. If finished, turn off the main power and pump it down.



Figure 4. O₂ plasma equipment used to clean the ITO patterned glass substrates.

2.3 Device Structure

Figure 5 shows the configuration of the different chemicals on the glass substrate. The devices are made using vacuum thermal evaporation.

Mg : Ag (10:1)
TPBI + 7% Cs ₂ CO ₃
TPBI
NPB
ITO
Glass

Figure 5. OLED device structure.

Table 2 explains the thickness of each layer for six different runs using the same configuration as in figure 5.

Table 2. Organic material thickness.

Samples	NPB (Å)	TPBI (Å)	TPBI + 7% Cs ₂ CO ₃ (Å)
1	750	600	0
2	750	600	300
3	750	300	300
4	750	300	500
5	750	300	750

The ITO in figure 5 acts as the anode while magnesium (Mg)/silver (Ag) acts as the cathode. The ratio in the Mg:Ag layer is 10 parts of Mg to 1 part of Ag. The thickness of the Mg:Ag varies on each device so that measurements can be performed to determine the devices' performance in terms of each one's operating voltage, current density, and luminance.

2.4 OLED Fabrication

Figure 6 shows the Trovato system used to fabricate OLED. The system consists of three main sections. The right side is a glove box with a thermal evaporator vacuum chamber. There are 16 boats controlled by 4 power supplies, which means the system can hold 16 different materials inside the vacuum chamber. Thus, all six substrates can be deposited at the same time. The second section is a vacuum transfer chamber. The purpose of the transfer chamber, as seen in figure 6, is to shuttle the devices and masks between the chamber and the glove box without having to lose vacuum to the deposition chamber. The glove box is attached directly to the transfer chamber to provide a clean, oxygen-free environment before, during, and after the device processes. The third section is left side of glove box, which contains a small mechanism that heats up glue and attaches a cap for encapsulation to keep air and moisture from affecting the OLED performance.



Figure 6. Equipment used to make OLED.

2.5 OLED Characterization

The OLED test equipment in figure 7 is used to test and measure different aspects of OLED performance, such as luminance level, power efficiency, and volts applied on the OLED, etc. This equipment is run by a program called LabView 8.5. The Photo Research PR650 is attached to the Keithley 2400, which collects the data and saves it into the computer program.

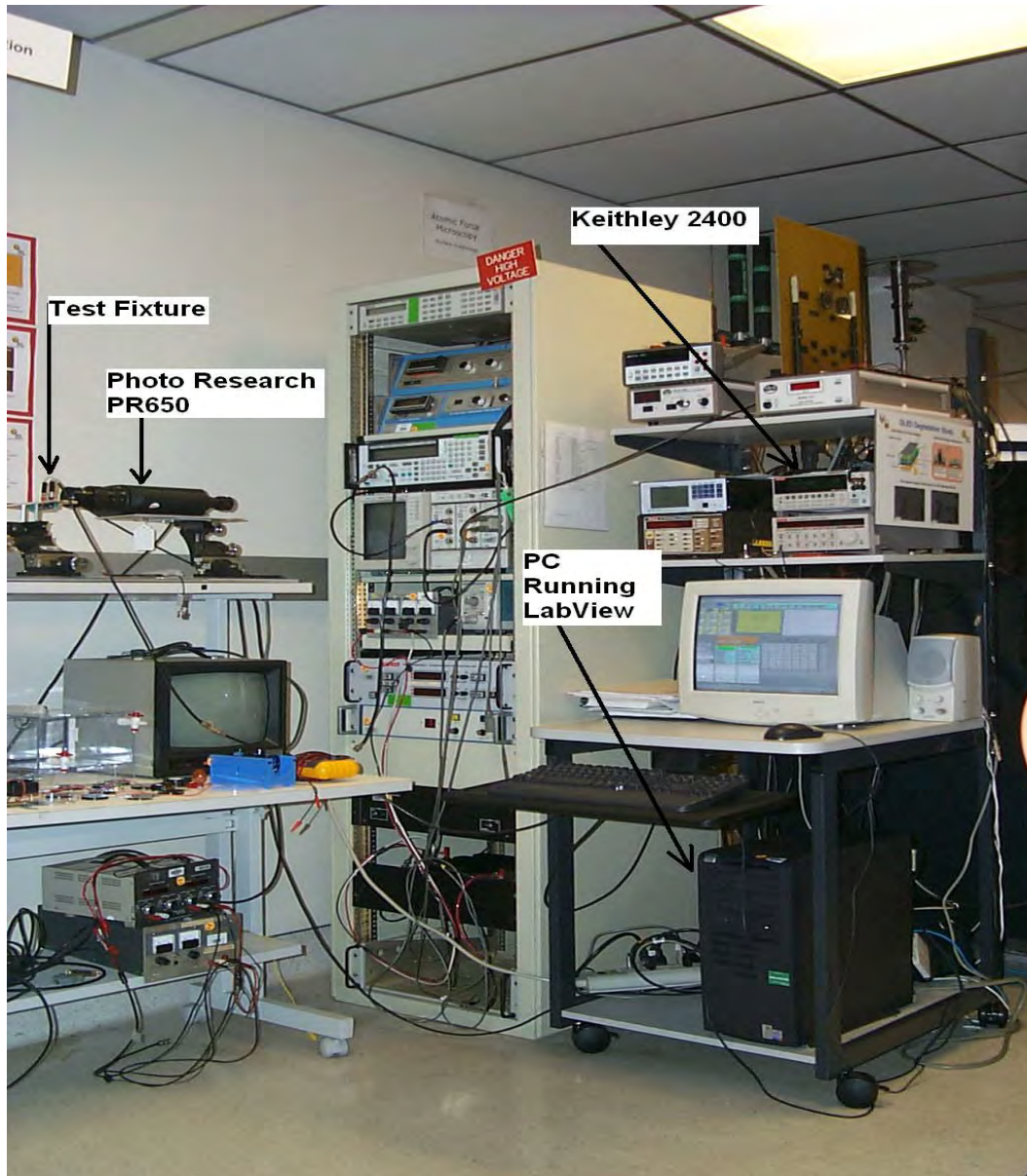


Figure 7. Equipment used to test and measure OLED (I).

To test an OLED, the following procedures should be used:

1. Open up LabView 8.5.
2. Insert an OLED into the slot, which is in front of the Photo Research PR650.
3. Change the scale to the preferred numbers.
4. Start the testing, and as the OLED lights up, center it in front of the camera.
5. When the Keithley 2400 says "OFF," the testing is over and a results sheet will appear on computer screen.

Figure 8 is a picture of the LabView 8.5 viewing front. As one runs the tests, the information shows up on this screen. The first column is current density J , which is measured in mA/cm^2 . The next column is the voltage needed to create the J . The third column is the luminance level, which is measured in cd/m^2 , followed by two calculated efficiency data columns, the CIE X and Y color coordinates. The three plots shown in the bottom left corner are the brightness-voltage (B-V) curve, the current-voltage (I-V) curve, and the brightness-current (B-I) curve. The two graphs above the table are the spectral plot, and the efficacy curve.

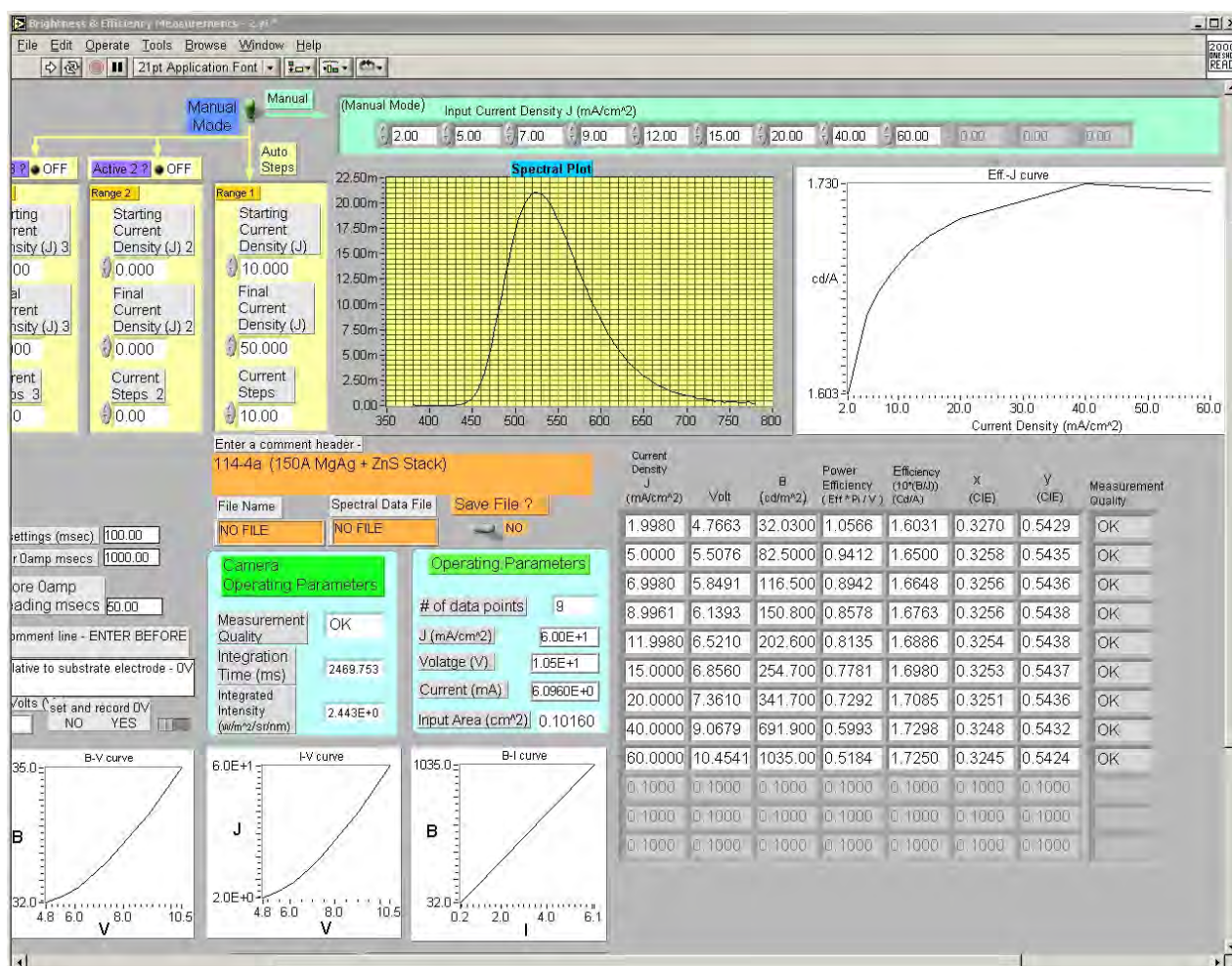


Figure 8. Example picture of LabView (I).

Figures 9 and 10 are images of a blue OLED under testing, showing a lit square blue pixel.

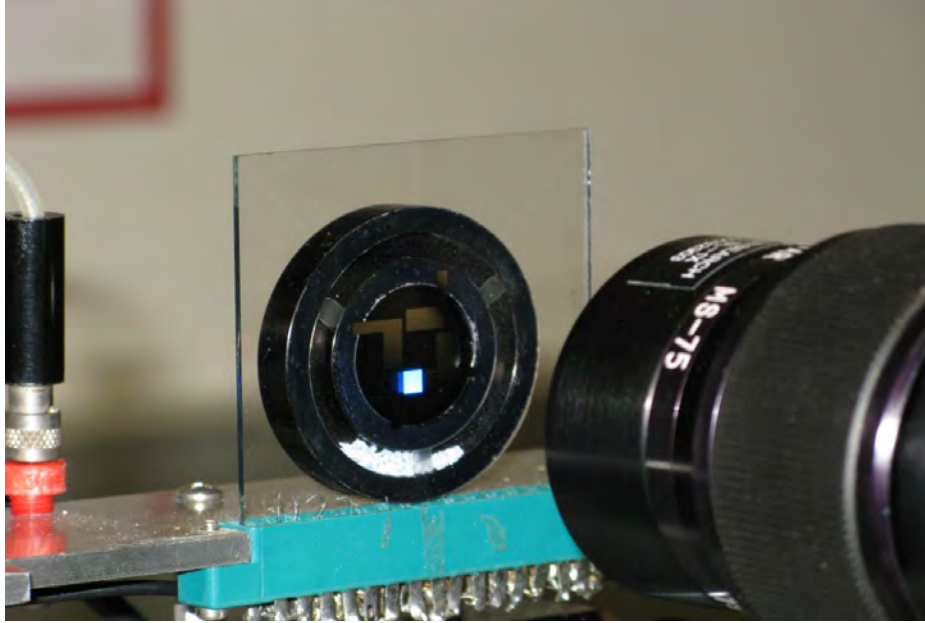


Figure 9. Front side of a blue OLED being tested.

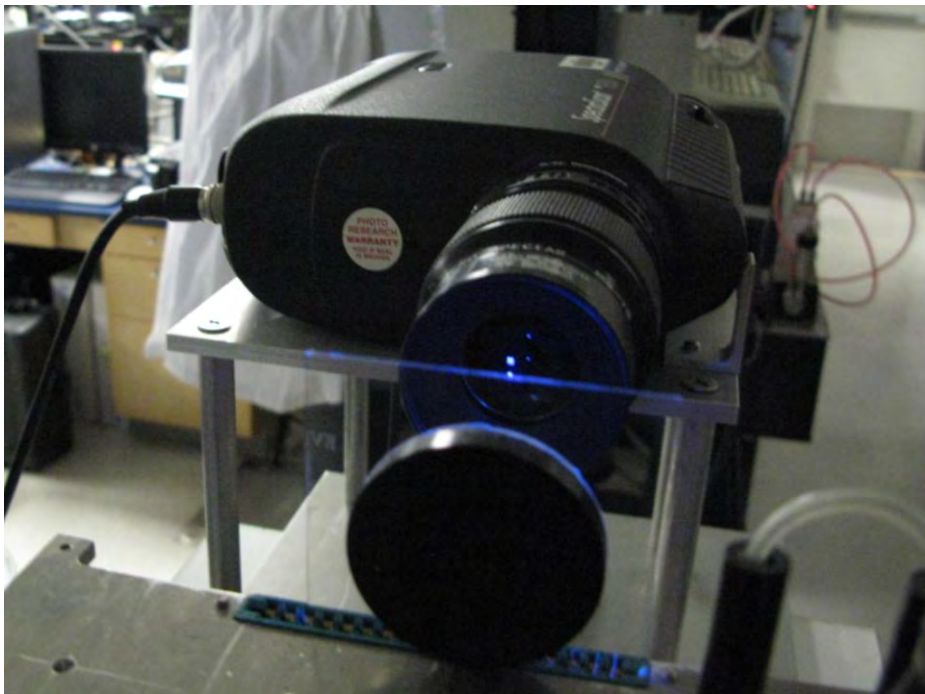


Figure 10. Back side of a OLED being tested (the black cap is placed there to keep any moisture from affecting the OLED).

3. Results and Discussion

Table 3 showed the blue OLED performance compared to another run of a blue OLED, which is shown in parentheses.

Table 3. Results of blue OLED measurement (all the numbers were taken from 20 mA/cm²).

Samples	Voltage (V)	B (cd/m ²)	CIE x	CIE y
NPB 750 Å/TPBI 600 Å	6.37 (6.44)	118 (116)	0.15 (0.16)	0.10 (0.10)
NPB 750 Å/TPBI 600 Å/ TPBI + 7% Cs ₂ CO ₃ 300 Å	6.09 (5.96)	66 (58)	0.16 (0.18)	0.23 (0.26)
NPB 750 Å/TPBI 300 Å/ TPBI + 7% Cs₂CO₃ 300 Å	4.87 (4.7)	133 (129)	0.16 (0.16)	0.10 (0.11)
NPB 750 Å/TPBI 300 Å/ TPBI + 7% Cs ₂ CO ₃ 500 Å	5.39 (4.75)	103 (97)	0.16 (0.16)	0.17 (0.17)
NPB 750 Å/TPBI 300 Å/ TPBI + 7% Cs ₂ CO ₃ 750 Å	5.14 (4.78)	31 (30)	0.20 (0.21)	0.22 (0.21)

Based on table 3, both batches achieved similar results consistently and showed that the NPB 750 Å/TPBI 300 Å/TPBI + 7% Cs₂CO₃ 300 Å recipe had the best results (lower voltage and higher luminance).

Figures 11 through 13 show evidence that all five recipes had low applied voltages for the blue OLEDs, but the device with the NPB 750 Å/TPBI 300 Å/ TPBI + 7% Cs₂CO₃ 300 Å recipe had the best performance. The ultimate goal is to have a low voltage with a high luminance (brightness). New material development is needed to keep a lower applied voltage and achieve a higher luminance.

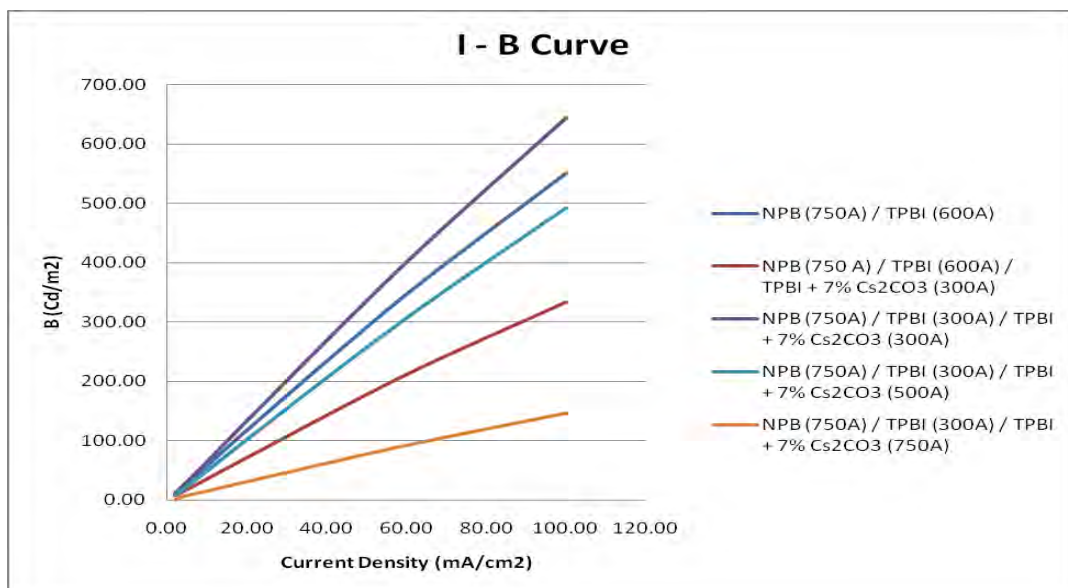


Figure 11. I-B graph.

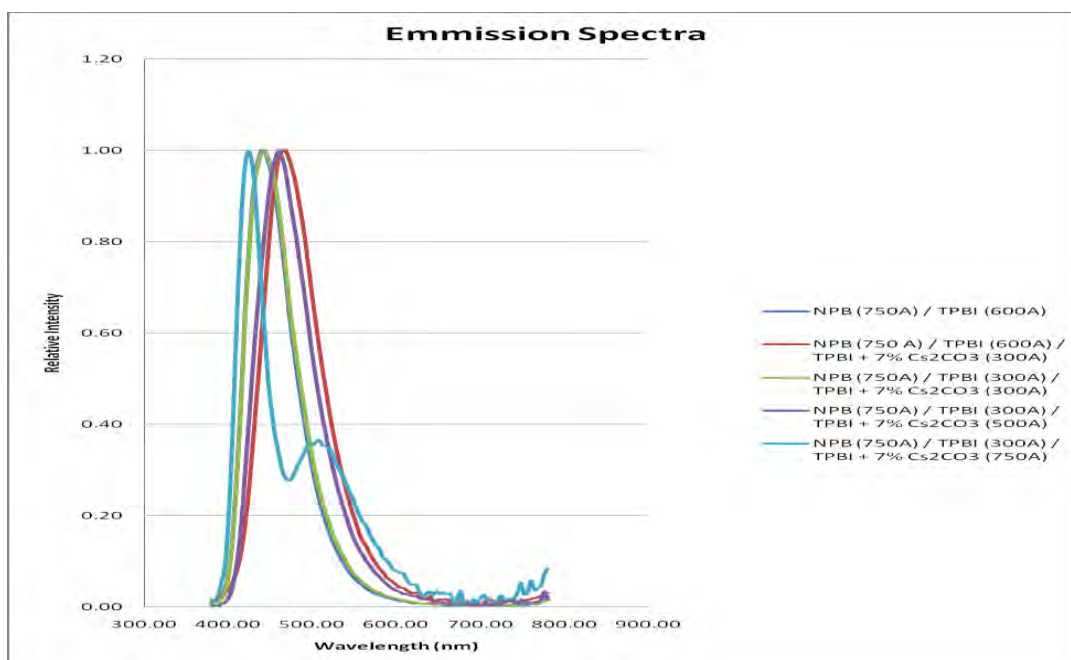


Figure 12. Emission spectra of the blue OLED.

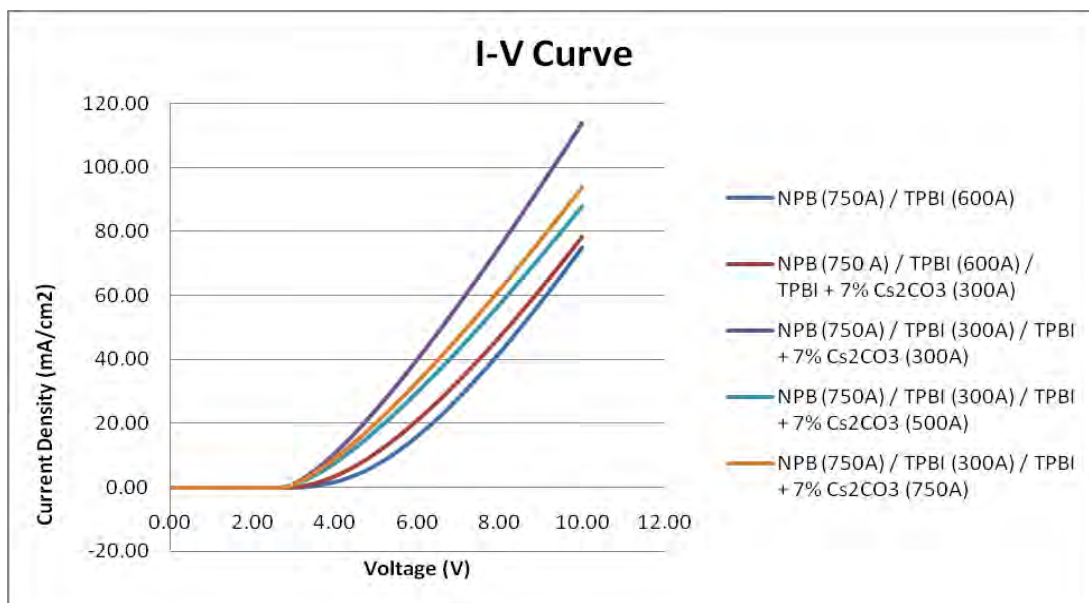


Figure 13. I-V curve.

4. Conclusions

The blue OLED ITO/TPBI/NPB/TPBI + 7%Cs₂CO₃/Mg:Ag device structure has been studied at different thickness levels of TPBI + 7% Cs₂CO₃ (0, 300, 500, and 700 Å). All blue OLEDs had low applied voltages, but the device with the NPB 750 Å/TPBI 300Å/TPBI + 7% Cs₂CO₃ 300 Å recipe had the best performance (the lowest voltage and the highest brightness).

New materials developments are under the way to keep a lower applied voltage and achieve a higher luminance with a full-color OLED display.

5. References

1. Chiu, D.; Blomquist, S.; Forsythe, E.; Shi, J.; Morton, D. *Characterization of Transparent Organic Light-Emitting Device (TOLED)*; ARL-TR-4322; U.S. Army Research Laboratory: Adelphi, MD, 2007.
2. Nguyen, T.; Destruel, P. Electroluminescent Devices Based on Organic Materials and Conjugated Polymers. *Handbook of Luminescence, Display Materials, and Devices*, 2003, 2–5.

List of Symbols, Abbreviations, and Acronyms

Ag	silver
ARL	U.S. Army Research Laboratory
B	brightness, cd/m^2
C	capacitance
CIE X	x color coordinate
CIE Y	y color coordinate
Cs_2CO_3	cesium carbonate
DI H_2O	deionized water
I	current
IPA	isopropyl alcohol
J	current density, mA/cm^2
ITO	indium tin oxide
Mg	magnesium
NPB	N,N'-Bis- (1-naphthalenyl)-N,N'-bis-phenyl-(1,1'-biphenyl)-4,4'-diamine
OLED	organic light emitting diodes
TPBI	1, 3, 5-Tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl
V	voltage

No. of Copies	Organization
1 ELEC	ADMNSTR DEFNS TECHL INFO CTR ATTN DTIC OCP 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218
3 HCS	US ARMY RSRCH LAB ATTN IMNE ALC HRR MAIL & RECORDS MGMT ATTN RDRL CIO LL TECHL LIB ATTN RDRL CIO MT TECHL PUB ADELPHI MD 20783-1197
17 HCS	US ARMY RSRCH LAB ATTN RDRL SEE E R FU (10 COPIES) ATTN RDRL SEE E E FORSYTHE ATTN RDRL SEE E J SHI ATTN RDRL SEE E S BLOMQUIST ATTN RDRL SEE E D MORTON ATTN RDRL SEE G WOOD ATTN RDRL SEE E K ALIBERTI ATTN RDRL SED E P PELLEGRINO 2800 POWDER MILL ROAD ADELPHI MD 20783-1197
TOTAL: 21 (1 ELEC, 20 HCS)	